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Structure and high-piezoelectricity in lead oxide solid solutions

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Abstract

A review of the recent advances in the understanding of piezoelectricity in lead oxide solid solutions is presented, giving special attention to the structural aspects. It has now become clear that the very high electromechanical response in these materials is directly related to the existence of low symmetry monoclinic phases. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Piezoelectricity; Phase diagram; Morphotropic phase boundary; PZT

1. Introduction

Understanding the mechanisms that produce the high piezoelectric response of the ceramic solid solution $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ (known as PZT) has been an issue since the 1950s when Shirane and co-workers [1,2] started the study of these materials. Much work has been done on PZT since then, mainly triggered by its importance in the electromechanical industry. PZT, with a piezoelectric coefficient of about 600 pm/V, one order of magnitude better than that of quartz, is the basis of most electromechanical devices in sonars, hydrophones, ultrasound generators, high-voltage generators, micropositioners, etc. [3].

The phase diagram of PZT was originally established in 1971 by Jaffe et al. [4] as shown (partially) in Fig. 1a. At high temperatures PZT has the cubic perovskite structure, with the lead atoms in the corners of the cubic unit cell, the zirconium/titanium atoms at the center of the cell and the oxygen atoms in the center of the cube faces, forming an octahedron. As the temperature is lowered, PZT undergoes a paraelectric-to-ferroelectric phase transition and the cubic unit cell is distorted due to the parallel ferroelectric shift of the cations with respect to the oxygen octahedra. The direction of the shifts is, however, different depending on the composition. For Ti-rich compositions the cations are displaced along the [001] direction and the symmetry becomes tetragonal. For Zr-rich compositions the cations are displaced along the [111] directions and the symmetry is rhombohedral. The most remarkable properties are those of compositions with $x \approx 0.50$, around the steep boundary

(with a change of 90 K per 1% Ti content) separating the rhombohedral and tetragonal regions, known as the morphotropic phase boundary (MPB), where the piezoelectric coefficients and dielectric constants exhibit an anomalously sharp maximum.

The exact location of the MPB was not previously well defined due to the existence of a phase coexistence region with an also poorly defined width. Different models have been proposed for the MPB: a finite region where both tetragonal and rhombohedral phases coexist, with the maximum of the dielectric and piezoelectric properties at the edges of the coexistence region [5,6]; a finite coexistence region in which one of the two phases is metastable [7]; and a true boundary, the observed coexistence region being explained either by unwanted compositional fluctuations [8], or by quenched-in thermal fluctuations [9]. This last work proposes the width of the coexistence region to be inversely proportional to the particle size, which means that an ideal boundary would be observed in the single crystal case (unfortunately, it is not possible to grow single crystals of PZT), and would explain the variety of widths observed experimentally in ceramic samples. Another subject of discussion among the piezoelectric community was whether the origin of the dielectric and piezoelectric anomalies observed at the MPB was intrinsic [10] or extrinsic (mainly due to domain wall motion).

That something was missing in our understanding of the MPBs and the physical properties associated with them it became especially clear after 1998, when Du et al., using a phenomenological approach, found a great enhancement of the piezoelectric response of rhombohedral PZT compositions oriented along [001], the tetragonal polar direction [11]. This was completely unforeseen since one

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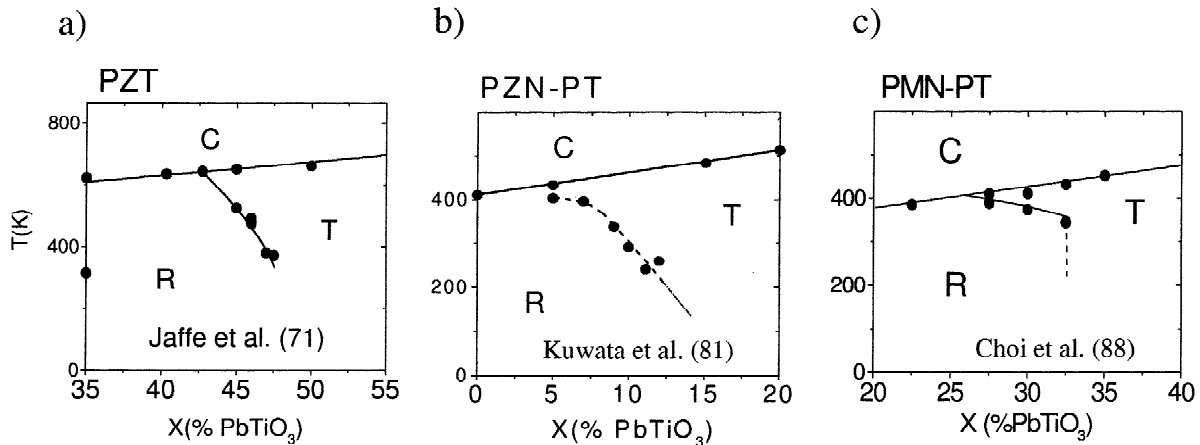


Fig. 1. (a) Phase diagram of $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ (PZT) around the morphotropic phase boundary (MPB) after Jaffe et al., adapted from Fig. 7.1 in Ref. [4]. (b) Phase diagram of $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3$ (PZN-xPT) after Kuwata et al., adapted from Fig. 5 in Ref. [13]. (c) Phase diagram of $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3$ (PMN-xPT) after Choi et al., adapted from Fig. 3 in Ref. [16].

expects the largest piezoelectric deformations to occur along the polar direction, which is determined by the symmetry axes ([001] for tetragonal samples and [111] for rhombohedral samples), implying that the electric field or stress needs to be applied along those directions in order to be efficient. But, on the other hand, a dependence of the piezoelectric response on the crystal orientation is something one definitely expects from the classical concept of piezoelectricity (see, e.g., Ref. [12]) and it is unfortunate that, due to the lack of single crystals of PZT, such studies have taken so long.

Kuwata et al., in the early 1980s [13], had already reported very high piezoelectric response in [001]-oriented single crystals of the relaxor-ferroelectric solid solution $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3$ (known as PZN-xPT). Later, Shrout et al. [14] also reported similar behavior in the related system $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3$ (known as PMN-xPT). But it was only recently when Park and Shrout [15] revived those works in a pioneering work which reported ultra-high electromechanical strain values attained in rhombohedral single crystals of PZN-xPT and PMN-xPT oriented along the [001] direction, and the potential of these systems in the next generation of electromechanical devices. This work also indicates that very high strain values can be achieved with little domain wall motion, displaying small non-linear effects, which is very interesting from the applications point of view. These properties were attributed to a so-called ‘engineered domain configuration’, in which multidomain [001]-oriented rhombohedral crystals result in a macroscopic tetragonal symmetry.

The phase diagrams of PZN-xPT [13] and PMN-xPT [16,17] (see Fig. 1b and c) are very similar to that of PZT (Fig. 1a), with a MPB in between the rhombohedral and tetragonal phases and, similar to PZT, had not been investigated at low temperatures. According to Park and Shrout [15] and Liu et al. [18], the very high electromechanical deformations in [001]-oriented rhombohedral crystal were related to an electric-field-induced phase transforma-

tion from the rhombohedral to the tetragonal phases. Durbin et al. [19] later confirmed this assertion by performing X-ray diffraction experiments on PZN-8% PT crystals with the electric field applied in situ along the [001] direction. They observed, first, that the microscopic strains exactly reflected the macroscopic strain measurements reported by Park and Shrout [15] and, second, that the lattice spacing observed along the [001] direction at high fields was that expected for the tetragonal compositions.

At approximately the same time, something unexpected happened: a monoclinic phase was observed by X-ray diffraction in PZT with a Ti content of 48% ($x=0.48$) [20–22], just at the MPB, in an extended temperature range between 20 and 300 K. This review is aimed at summarizing the most relevant work published about high-piezoelectric solid solutions with MPBs following the discovery of the monoclinic phase, which has notably changed our perception of piezoelectric materials. Some issues that have become more controversial in the last months and still need to be clarified will also be discussed.

2. New phase diagrams: the intermediate monoclinic phases

The monoclinic phase observed in PZT with $x=0.48$ has subsequently been observed for neighboring compositions with $0.45 < x < 0.52$, and a new phase diagram has been reported [23]. The monoclinic region forms a narrow triangle in between the tetragonal and rhombohedral phases (see Fig. 2a), with an essentially vertical rhombohedral–monoclinic boundary and a slightly slanted tetragonal–monoclinic boundary, which agrees very well with the original MPB reported by Jaffe et al. [4] above room temperature.

The structure determination for the $x=0.48$ composition, which is tetragonal above room temperature and mono-

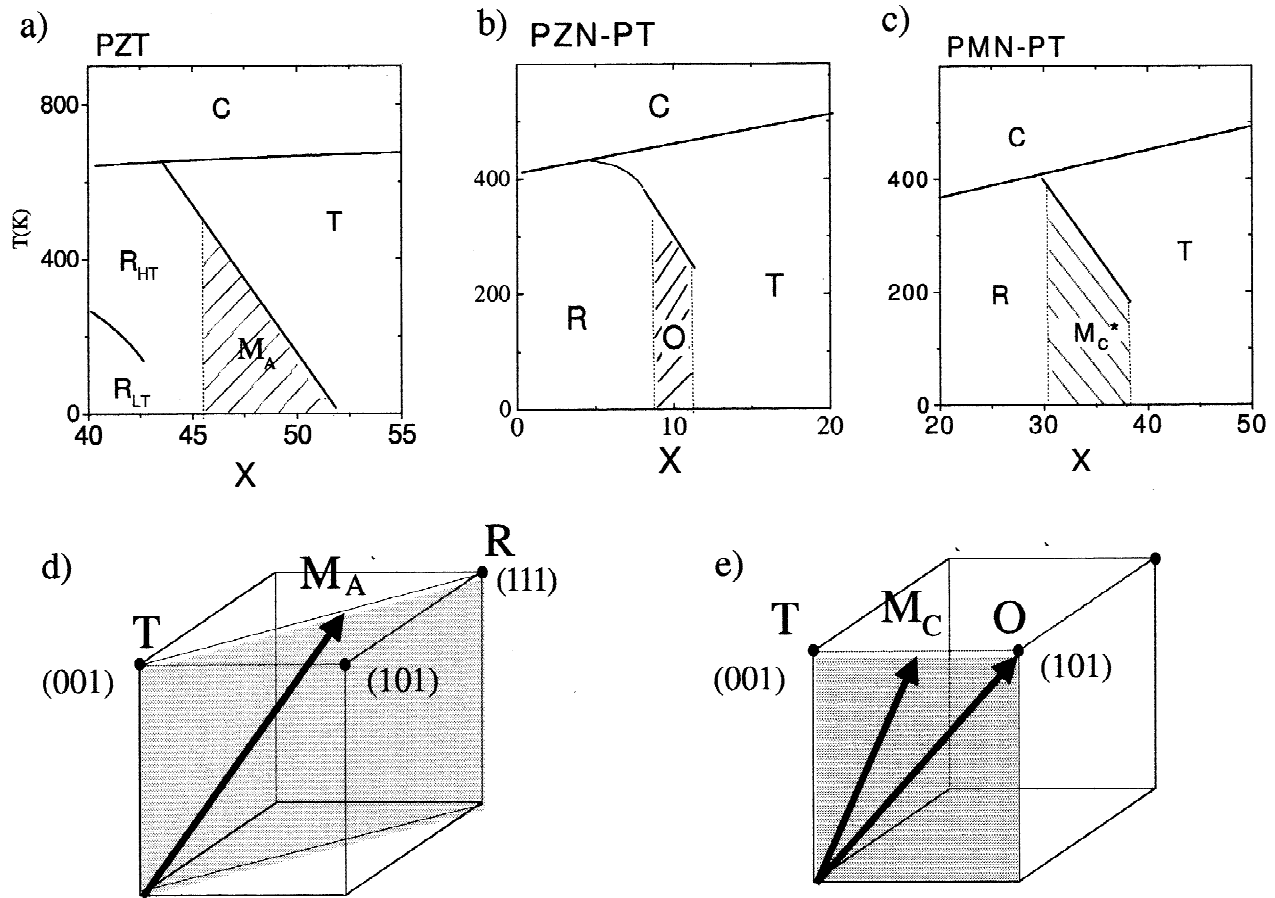


Fig. 2. (a) New phase diagram of PZT around the MPB, adapted from Fig. 6 in Ref. [23]. (b) New phase diagram of PZN-xPT, adapted from Fig. 7 in Ref. [40]. (c) New phase diagram of PMN-xPT, adapted from Fig. 10 in Ref. [50]. (d) Sketch of the perovskite unit cell with the polarization vector (solid arrow) in the monoclinic M_A phase, rotating between the rhombohedral (R) and tetragonal (T) phases in the $(1\bar{1}0)$ plane (shaded). (e) Sketch of the perovskite unit cell with polarization vectors (solid arrows) in the monoclinic M_C and orthorhombic (O) phases, rotating in the (010) plane (shaded).

clinic below room temperature, has been reported from synchrotron X-ray diffraction data [24]. The monoclinic unit cell (a_m , b_m , c_m , β) is rotated 45° about the c -axis with respect to the tetragonal one; that is, a_m and b_m lie along the face diagonals of the prism base, and c_m is practically equal to the tetragonal c_t , but tilted a small angle $90^\circ - \beta$ with respect to it. The atomic positions have been obtained for the tetragonal (space group $P4mm$, $T=325$ K) and monoclinic (space group Cm , $T=20$ K) phases for this composition and it has been demonstrated that the tetragonal phase transforms into the monoclinic one by shifts of the Pb and Zr/Ti cations along the tetragonal $[110]$ direction [24]. The monoclinic plane (defined by a_m and c_m) is the only symmetry element, and contains the polar axis of both the tetragonal and rhombohedral phases. It has been found that the monoclinic polarization is also contained in the monoclinic plane, pointing along a direction in between $[001]$ and $[111]$ [24].

This fact turns out to be the key to understanding the anomalously high piezoelectric response in PZT and, in general (as will be shown later), in all systems with MPBs. By symmetry reasons, the polarization vector in the

monoclinic phase is constrained to lie in the monoclinic plane, but otherwise is free to rotate within it. The monoclinic phase represents the structural bridge between the tetragonal (space group $P4mm$) and the rhombohedral (space group $R3m$) phases through the common symmetry element, the mirror or monoclinic plane (m) [24] (see Fig. 2d). This ease rotation is reflected by the very high values of the piezoelectric coefficient, as calculated by Bellaiche et al. [25] and Fu and Cohen [26] from first principles (for more details, see the review by Bellaiche in this issue). According to these calculations [25], the polarization vector can rotate continuously within the monoclinic phase as a function of composition. Moreover, as shown by Topolov and Turik, this phase also allows for the relief of internal stresses and provides elastic matching at the MPB [27]. The monoclinic phase in PZT has also been observed by Raman spectroscopy [28,29], X-ray diffraction and dielectric measurements [30], and neutron diffraction [31–33] (see also Discussion section).

This is the first example of ferroelectric monoclinic perovskites with polarization components $P_x = P_y \neq P_z$, as predicted by Shuvalov in 1970 [34]. Other than this, the

existence of a monoclinic ferroelectric perovskite had not been considered before, most likely because the sixth-order Devonshire expansion of the free energy previously used successfully to describe ferroelectric perovskites, in particular PZT [10,35,36], could not however account for monoclinic phases. Vanderbilt and Cohen [37] have recently solved this problem, showing that an *eighth-order* Devonshire expansion generates monoclinic ferroelectric perovskites, and that even triclinic ones can be obtained by a twelfth-order expansion of the free energy.

Three different monoclinic phases are predicted by this approach: M_A , the one observed in PZT, with a $(1\bar{1}0)$ mirror plane and $c > a$ and b ; M_B , similar to M_A but with $c < a$ and b ; and M_C , with a (010) mirror plane, respectively. Of these three, only M_B remains unobserved, since the M_C phase has now been observed in PZN-8% PT under an applied electric field, and in PMN-xPT at zero field, as described in the next section.

Since the existence of a monoclinic phase seems to be directly related to the observation of high piezoelectric coefficients, it is not surprising to find such a phase around the MPBs of the PZN-xPT and PMN-xPT systems. Indications of symmetry lowering attributed to a *hetero-phase coexistence* had been reported by Uesu et al. [38] based on optical measurements, and synchrotron X-ray powder diffraction studies performed on ground PZN-xPT single crystals [39–41] have shown the presence of an intermediate phase. The latter has two interesting features; first, it exists only in a very narrow compositional range between $0.08 < x < 0.11$ and, second, it has *orthorhombic* (O) symmetry, as shown in Fig. 2b. In agreement with the new phase diagram [40], no lowering of symmetry was found in PZN-4.5% PT [42]. Neutron powder data reported by Kiat et al. [43] show very similar features but it has been interpreted in terms of a monoclinic M_C structure rather than orthorhombic.

A phase diagram with an intermediate orthorhombic phase has already been proposed from a phenomenological approach [35], and such an orthorhombic phase, with space group $Amm2$, is in principle identical to that of the well-known ferroelectric $BaTiO_3$. However, there is a basic difference between those two: orthorhombic $BaTiO_3$ is *not* at a MPB. In *morphotropic* orthorhombic PZN-xPT, the monoclinic M_C phase is extremely close in energy, and a very small electric field applied in the $[001]$ direction is enough to induce the monoclinic phase, in which the polarization can rotate between the orthorhombic (O) and tetragonal (T) phases (see Fig. 2e), as will be discussed in more detail in the next section. Neutron diffraction measurements on four different PZN-9% PT single crystals [44] have shown that, while three of them were O, as in Ref. [39], one of them displayed the M_C phase, another indication the O and M_C free energies are nearly degenerate [45], and it is indeed necessary to consider higher-order terms in the Devonshire expansion to determine the

stability of one or the other [37]. The M_C and O symmetries can be especially difficult to resolve because O is the limiting case of M_C with $a_m = c_m$ [46].

A structure determination of PZN-9% PT by means of Rietveld refinement from neutron powder diffraction data has been reported by Kiat et al. [43] who show that, while the oxygen octahedra are strongly distorted, the cation displacements and the polarization values of monoclinic PZN-9% PT (M_C) are considerably smaller than those of monoclinic PZT (M_A) [24] and, unlike PZT, the direction of the Pb and Zn/Nb/Ti cation shifts is not the same.

A fascinating domain formation is reported to occur also in morphotropic PMN-xPT [47,48] (see review by Ye in this issue). Xu et al. [48] have observed monoclinic domains coexisting with rhombohedral domains in a PMN-33PT crystal. Interestingly, this monoclinic phase is not unique and various polarization directions have been observed within the same crystal. The existence of an M_C type of monoclinic phase has been reported by Kiat et al. [43] in ceramic PMN-35PT at low temperature, and by Singh and Pandey [49] in ceramic PMN-34PT at room temperature, from a Rietveld analysis of neutron and X-ray powder diffraction data, respectively. Based on the atomic shifts obtained from the Rietveld analysis, Kiat et al. [43] have reported a very small value of the spontaneous polarization for the PMN-35% PT composition, considerably smaller than that of *morphotropic* PZT and PZN-xPT, which is not in agreement with the experimental observation [16].

Very recent synchrotron X-ray powder diffraction measurements performed on PMN-xPT ceramic samples [50] have revealed a new phase diagram for the PMN-xPT system, shown in Fig. 2c, in which the M_C monoclinic phase exists at the MPB, with an apparently rather broad distribution of monoclinic lattice parameters. However, in contrast to Refs. [43,49], the monoclinic phase always appears in coexistence with either rhombohedral or tetragonal phases. This phase coexistence might account for the substantial differences between the atomic positions listed in Refs. [43,49].

3. Electric-field-induced monoclinic phases

The enhancement of the piezoelectric deformation along the $[001]$ direction, proposed by Du et al. [11] in rhombohedral PZT, has now been observed in both thin films [51] and ceramics [52,53]. The fact that the piezoelectric deformation is not along the rhombohedral polar direction has been interpreted by Guo et al. as due to the induction of the monoclinic phase by the electric field [52]. These authors also show that the induced monoclinic phase remains stable after the field is removed, so the rhombohedral-to-monoclinic phase change is irreversible. This can be explained in relation to the local monoclinic

displacements that are believed to exist in rhombohedral PZT (see Refs. [24,54]), since an electric field along the [001] direction would favor local shifts along that direction and, therefore, stabilize a long-range monoclinic phase in the rhombohedral region of the phase diagram. This seems to be a common feature in *morphotropic* systems and the same kind of local displacements have been reported by Dkhil et al. [55] in rhombohedral PMN-PT.

X-ray diffraction experiments by Durbin et al. [56] on a PZN-8% PT single crystal poled along the [001] direction showed that the electric field induces a new state, different from the initial rhombohedral one, which they interpreted as a metastable monoclinic phase induced by the coexistence of tetragonal and rhombohedral regions. Synchrotron X-ray [57,58], and neutron [59] diffraction experiments with the electric field applied in situ, have given a consistent picture of the field effect in [001]-oriented rhombohedral PZN-xPT. For compositions further away from the MPB (PZN-4.5% PT) the rhombohedral-to-tetragonal phase transformation proposed earlier [15,18] is observed to occur via the M_A phase (R– M_A –T), as predicted by Fu and Cohen [26] from first-principles calculations, with the polarization rotating directly between the [111] and [001] directions within the (110) plane (Fig. 2d). However, for rhombohedral compositions close to the MPB (PZN-8% PT), a *different* path is followed, namely R– M_A – M_C –T. This means the polarization moves away from the R– M_A –T line onto the O– M_C –T line, in which the polarization rotates between the [101] (O) and the [001] (T) directions (Fig. 2e). This observation agrees with the first-principles calculations by Bellaiche et al. [60] in the case of morphotropic PZT. These authors also predict that the crossover between the M_A and M_C phases is achieved via a triclinic phase (see also the review by Bellaiche in this issue). The largest piezoelectric coefficients are associated with the triclinic phase.

The synchrotron experiments [57,58] also show that, once the electric field is applied on PZN-8% PT, the initial rhombohedral phase is not recovered. The polarization follows the T– M_C –O path during the removal of the field, with the polarization rotating back from the [001] to the [101] direction, and the orthorhombic phase becomes stable at zero field. Therefore, an irreversible rhombohedral–orthorhombic phase change takes place under a field, meaning that the intermediate phase in the PZN-PT phase diagram is enlarged towards smaller Ti contents, as in PZT. These results agree with the work of Viehland [61], who was the first to report an orthorhombic phase for poled PZN-8% PT.

Viehland's work also presents an alternative explanation of the rhombohedral-to-tetragonal phase transformation as a continuous sequence of *mesostates* that occur by symmetry adaptations, similar to those predicted by the adaptive martensite theory, which involves a model of a free energy with a continuous sequence of degenerate states [61].

Later, Lu et al. [62] and Viehland et al. [63] have shown that very high piezoelectricity is not exclusive of <001>-oriented crystals, but can also be achieved in <011>-oriented PZN-xPT and PMN-xPT rhombohedral crystals, by inducing the orthorhombic phase instead of the tetragonal one. This is highly significant, since the polarization path in this case would very likely be the R– M_B –O one, and the M_B phase has not been observed so far.

The effect of an electric field on PMN-xPT has not been studied as extensively. In addition to the M_C -type monoclinic phase observed in the PMN-xPT phase diagram [43,49,50], and the orthorhombic phase proposed for <011>-poled crystals [62,63], Ye et al. [64] also observed a monoclinic M_A phase in a <001>-poled PMN-35% PT single crystal. How the M_C – M_A transformation between the two monoclinic phases takes place under a field has still not been studied in detail.

4. Discussion

Much progress has been achieved during the last three years in understanding the high piezoelectricity around the MPBs, as well as other features of some of these systems that are outside of the scope of this review, such as their relaxor character and the nature of the polar nano-regions (see, e.g., Ref. [65] and references therein). However, more research is still needed; in particular, in the following two areas: (1) the investigation of the role of lead on the softening of the physical properties of these materials [66,67], not only for fundamental reasons, but also in order to explore new possibilities with lead-free systems (see review by Park and Hackenberger in this issue); (2) the study of rotational lattice distortions, as initiated by Fornari and Singh [68].

X-ray diffraction provides a high-resolution tool to resolve the slight symmetry changes observed around the MPBs, but X-rays are not very sensitive to small distortion of the oxygen octahedra in the presence of other atoms with high atomic numbers. In the case of PZT, electron [30] and neutron [32,33,69] diffraction have been able to observe superlattice reflections at low temperatures around the MPB, which were not revealed by X-rays. The same types of superlattice reflections are known to occur in the rhombohedral R_{LT} phase [70] at low temperatures (see Fig. 2a), and are related to the cell doubling produced by the rotation of the oxygen octahedra about the [111] direction. Since these reflections are not consistent with the M_A phase (space group Cm), two different models have been proposed on the basis of a Rietveld analysis of the neutron data: the existence of a second low-temperature monoclinic phase with space group Pc [69], and the coexistence of the M_A monoclinic phase and the R_{LT} (space group R3c) rhombohedral phase [32,33], whose boundary with the monoclinic phase towards higher Ti contents is still not

determined. The absence of superlattice reflections in some of the grains, recently observed by electron microscopy,¹ strongly supports the coexistence scenario proposed by Frantii et al. [32,33]; namely, that, at low temperatures (10 K), 86% of a PZT ($x=0.48$) sample is monoclinic M_A while the remaining 14% is in the rhombohedral R_{LT} phase, which also explains the weakness of the superlattice reflections observed in the neutron patterns. The latter authors also report an increment of the amount of R_{LT} phase for lower Ti content (29% for $x=0.47$), consistent with the proximity of the R_{LT} boundary in that direction. This coexistence picture is in agreement with calculations by Fornari and Singh [68] mentioned above, who predict a deep instability of the rotational degrees of freedom, comparable to the ferroelectric one.

5. Conclusions

The MPB is defined as the steep boundary where two neighboring phases in the phase diagram are degenerate, and is often observed in real systems as a finite region of phase coexistence. This very special feature produces ‘soft’ materials with very interesting dielectric and electromechanical properties. An up-to-date picture of the MPBs of PZT and related systems shows that the phase coexistence region can be resolved in highly homogeneous samples, and that the tetragonal and rhombohedral phases are not really degenerate. Instead of a boundary, a third phase with lower symmetry lies in between the two regions, ‘loosening’ the polarization and ‘softening’ the material. Ultimately, one could imagine an ideal MPB in an even more anharmonic system with a *triclinic* phase at the MPB, where the polarization would be completely free and the dielectric and piezoelectric coefficients would be maximized. It may not be so long before the search for even better electromechanical materials will reveal such a system.

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References

- [1] Shirane G, Takeda A. Phase transitions in solid solutions of $PbZrO_3$ and $PbTiO_3$: I. Small concentrations of $PbTiO_3$. J Phys Soc Jpn 1952;7:5–11;
- [2] Shirane G, Suzuki K. Crystal structure of $Pb(Zr-Ti)O_3$. J Phys Soc Jpn 1952;7:333.
- [3] See, e.g., Xu Y. Ferroelectric materials and their applications. Amsterdam: North-Holland, 1991.
- [4] Jaffe B, Cook WR, Jaffe H, editors. Piezoelectric ceramics, London: Academic Press, 1971, pp. 135–83.
- [5] Ari-Gur P, Benguigui L. Direct determination of the coexistence region of solid solutions $Pb(Zr_xTi_{1-x})O_3$. J Phys D Appl Phys 1975;8:1856–62.
- [6] Mishra SK, Pandey D, Singh AP. Effect of phase coexistence at morphotropic phase boundary on the properties of $Pb(Zr_xTi_{1-x})O_3$ ceramics. Appl Phys Lett 1996;69:1707–9.
- [7] Isupov VA. Comments on the paper ‘X-ray study of the PZT solid solution near the morphotropic phase transition’. Solid State Commun 1975;17:1331–3.
- [8] Kakegawa K, Mohri J, Takahashi T, Yamamura H, Shirasaki S. Compositional fluctuation and properties of $Pb(Zr,Ti)O_3$. Solid State Commun 1977;24:769–72.
- [9] Cao W, Cross LE. Theoretical model for the morphotropic phase boundary in lead zirconate–titanate solid solution. Phys Rev B 1993;47:4825–30.
- [10] Ishibashi Y, Iwata M. Morphotropic phase boundary in solid-solution systems of perovskite-type oxide ferroelectric. Jpn J Appl Phys 1998;37:L985–7.
- [11] Du X-H, Zheng J, Belegundu U, Uchino K. Crystal orientation dependence of piezoelectric properties of lead zirconate titanate near the morphotropic phase boundary. Appl Phys Lett 1998;72:2421–3.
- [12] Nye JF. Physical properties of crystals, 2nd ed.. Oxford: Clarendon Press, 1985.
- [13] Kuwata J, Uchino K, Nomura S. Phase transitions in the $Pb(Zn_{1/3}Nb_{2/3})O_3$ – $PbTiO_3$ system. Ferroelectrics 1981;37:579–82.
- [14] Shrout T, Chang ZP, Kin M, Markgraf S. Dielectric behavior of single crystals near the $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$ – $xPbTiO_3$ morphotropic phase boundary. Ferroelec Lett 1990;12:63–9.
- [15] Park S-E, Shrout TR. Ultrahigh strain and piezoelectric behavior in relaxor based ferroelectric single crystals. J Appl Phys 1997;82:1804–11.
- [16] Choi SW, Shrout TR, Jang SJ, Bhalla AS. Dielectric and pyroelectric properties in the $Pb(Mg_{1/3}Nb_{2/3})O_3$ – $PbTiO_3$ systems. Ferroelectrics 1989;100:29–38.
- [17] Noblanc O, Gaucher P, Calvarin G. Structural and dielectric studies of $Pb(Mg_{1/3}Nb_{2/3})O_3$ – $PbTiO_3$ ferroelectric solid solutions around the morphotropic phase boundary. J Appl Phys 1996;79:4291–7.
- [18] Liu S-F, Park S-E, Shrout TR, Cross LE. Electric field dependence of piezoelectric properties for rhombohedral $0.955Pb(Zn_{1/3}Nb_{2/3})O_3$ – $0.045PbTiO_3$ single crystals. J Appl Phys 1999;85:2810–4.
- [19] Durbin MK, Jacobs EW, Hicks JC. In situ X-ray diffraction study of an electric field induced phase transition in the single crystal relaxor ferroelectric $92\%Pb(Zn_{1/3}Nb_{2/3})O_3$ – $8\%PbTiO_3$. Appl Phys Lett 1999;74:2848–50.
- [20] Noheda B, Cox DE, Shirane G, Gonzalo JA, Cross LE, Park S-E. A monoclinic ferroelectric phase in the $Pb(Zr_{1-x}Ti_x)O_3$ solid solution. Appl Phys Lett 1999;74:2059–61.
- [21] Noheda B, Gonzalo JA, Caballero AC, Moure C, Cox DE, Shirane G. New features of the morphotropic phase boundary in the $Pb(Zr_{1-x}Ti_x)O_3$ system. Ferroelectrics 2000;237:237–44.
- [22] Noheda B, Gonzalo JA, Guo R, Park S-E, Cross LE, Cox DE et al. The monoclinic phase in PZT: new light on morphotropic phase boundaries. In: Cohen R, editor, Fundamental physics of ferroelectrics, New York: AIP, 2000, pp. 304–13.
- [23] Noheda B, Cox DE, Shirane G, Guo R, Jones B, Cross LE. Stability of the monoclinic phase in the ferroelectric perovskite $PbZr_{1-x}Ti_xO_3$. Phys Rev B 2001;63:014103/1–6.

¹Noheda B, Lijun W, Zhu Y. Origin of the low temperature superlattice reflections in monoclinic PZT (to be published).

- [24] Noheda B, Gonzalo JA, Cross LE, Guo R, Park S-E, Cox DE et al. Tetragonal-to-monoclinic phase transition in a ferroelectric perovskite: the structure of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$. *Phys Rev B* 2000;61:8687–95.
- [25] Bellaiche L, Garcia A, Vanderbilt D. Finite-temperature properties of $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ alloys from first principles. *Phys Rev Lett* 2000;84:5427–30.
- [26] Fu H, Cohen RE. Polarization rotation mechanism for ultrahigh electromechanical response in single-crystal piezoelectrics. *Nature* 2000;403:281–3.
- [27] Topolov VY, Turik AV. A new monoclinic phase and features of stress relief in $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$. *J Phys Condens Matter* 2001;13:L771–5.
- [28] Souza Filho AG, Lima KCV, Guedes I, Freire PTC, Mendes Filho J, Araujo EB et al. Monoclinic phase in $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ ceramics: Raman and phenomenological thermodynamic studies. *Phys Rev B* 2000;61:14283–6.
- [29] Lima KCV, Souza Filho AG, Ayala AP, Mendes Filho J, Freire PTC, Melo FEA et al. Raman study of the morphotropic phase boundary in $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$. *Phys Rev B* 2001;63:184105/1–5.
- [30] Ragini S, Dhananjai P, Lemmens H, Van Tendeloo G. Evidence for another low-temperature phase transition in tetragonal $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ ($x=0.515, 0.520$). *Phys Rev B* 2001;054101/1–6.
- [31] Mmowski W, Egami T, Farber L, Davies PK. Structure of $\text{Pb}(\text{Zr,Ti})\text{O}_3$ near the morphotropic phase boundary. In: Krakauer H, editor. *Fundamental physics of ferroelectrics*, New York: AIP, 2001, pp. 33–44.
- [32] Frantii J, Ivanov S, Eriksson S, Lappalainen J, Lantto V, Kakihana M et al. Neutron diffraction and bond valence calculation studies of $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ ceramics. *Ferroelectrics* (in press).
- [33] Frantii J, Ivanov S, Rundlof H, Lantto V, Lappalainen J, Kakihana M. On the phase transitions of $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ ceramics (private communication).
- [34] Shuvalov LA. Symmetry aspects of ferroelectricity. *J Phys Soc Jpn* 1970;28:38–51.
- [35] Haun MJ, Furman E, Jang SJ, Cross LE. Thermodynamic theory of the lead zirconate–titanate solid solution system: I. Phenomenology. *Ferroelectrics* 1989;99:13–25.
- [36] Ishibashi Y, Iwata M. A theory of morphotropic phase boundaries in solid-solution systems of perovskite-type oxide ferroelectric. *Jpn J Appl Phys* 1999;38:800–4.
- [37] Vanderbilt D, Cohen MH. Monoclinic and triclinic phases in higher-order Devonshire theory. *Phys Rev B* 2001;63:094108/1–9.
- [38] Uesu Y, Yamada Y, Fujishiro K, Tazawa H, Enokido S, Kiat J-M et al. Structural and optical studies of development of the long-range order in ferroelectric relaxor $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ /9% PbTiO_3 . *Ferroelectrics* 1998;217:319–25.
- [39] Cox DE, Noheda B, Shirane G, Uesu Y, Fujishiro K, Yamada Y. Universal phase diagram for high-piezoelectric perovskite systems. *Appl Phys Lett* 2001;79:400–2.
- [40] La-Orautapong D, Noheda B, Ye Z-G, Gehring PM, Toulouse J, Cox DE et al. New phase diagram of the relaxor ferroelectric $(1-x)\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $x\text{PbTiO}_3$. *Phys Rev B* 2002;65:144101/1–7.
- [41] Noheda B, Cox DE, Shirane G. Low symmetry phases in piezoelectric systems: PZN-PT single crystal and powder. *Ferroelectrics* (in press).
- [42] Forrester JS, Piltz RO, Kisi EH, McIntyre GJ. Temperature-induced phase transitions in the giant-piezoelectric-effect material PZN-4.5% PT. *J Phys Condens Matter* 2001;13:L825–33.
- [43] Kiat J-M, Uesu Y, Dkhil B, Matsuda M, Malibert C, Calvarin G. Monoclinic structure of unpoled PMN-PT and PZN-PT compounds. *Phys Rev B* 2002;65:064106/1–4.
- [44] Uesu Y, Matsuda M, Yamada Y, Fujishiro K, Cox DE, Noheda B et al. Symmetry of high-piezoelectric Pb based complex perovskites at the morphotropic phase boundary: I. Neutron diffraction study on $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ -9% PbTiO_3 . *J Phys Soc Jpn* 2002;71:960–5.
- [45] Yamada Y, Uesu Y, Matsuda M, Fujishiro K, Cox DE, Noheda B et al. Symmetry of high-piezoelectric Pb based complex perovskites at the morphotropic phase boundary: II. Theoretical treatment. *J Phys Soc Jpn* 2002;71:966–70.
- [46] Noheda B, Cox DE, Shirane G, Park S-E, Cross LE, Zhong Z. Polarization rotation via a monoclinic phase in the piezoelectric 92% $\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3$ -8% PbTiO_3 . *Phys Rev Lett* 2001;86:3891–4.
- [47] Ye Z-G, Dong M. Morphotropic domain structures and phase transitions in relaxor-based piezo-/ferroelectric $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $x\text{PbTiO}_3$ single crystals. *J Appl Phys* 2000;87:2312–9.
- [48] Xu G, Luo H, Xu H, Yin Z. Third ferroelectric phase in PMNT single crystals near the morphotropic phase boundary composition. *Phys Rev B* 2001;64:020102/1–3.
- [49] Singh AK, Pandey D. Structure and the location of the morphotropic phase boundary in $(1-x)[\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3]$ - $x\text{PbTiO}_3$. *J Phys Condens Matter* 2001;13:L931–6.
- [50] Noheda B, Cox DE, Shirane G, Dong M, Ye Z-G, Gao J. Phase diagram of the ferroelectric-relaxor $(1-x)\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ - $x\text{PbTiO}_3$. *Phys Rev B* (submitted for publication). *Cond-matt/0203422*.
- [51] Taylor DV, Damjanovic D. Piezoelectric properties of rhombohedral $\text{Pb}(\text{Zr,Ti})\text{O}_3$ thin films with (100), (111) and ‘random’ crystallographic orientation. *Appl Phys Lett* 2000;76:1617–25.
- [52] Guo R, Cross LE, Park S-E, Noheda B, Cox DE, Shirane G. Origin of the high piezoelectric response in $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$. *Phys Rev Lett* 2000;84:5423–6.
- [53] Reszat J-T, Glazonounov AE, Hoffmann MJ. Analysis of intrinsic lattice deformation in PZT-ceramics of different compositions. *J Eur Ceram Soc* 2001;21:1349–52.
- [54] Corker DL, Glazer AM, Whatmore RW, Stallard A, Fauth F. A neutron diffraction investigation into the rhombohedral phases of the perovskite series $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$. *J Phys Condens Matter* 1998;10:6251–69.
- [55] Dkhil B, Kiat J-M, Calvarin G, Baldinozzi G, Vakhurshev SB, Suard E. Local and long range order in the relaxor-ferroelectric compounds $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ and $\text{PbMg}_{0.3}\text{Nb}_{0.6}\text{O}_3$. *Phys Rev B* 2002;65:024204/1–8.
- [56] Durbin MK, Hicks JC, Park S-E, Shrout TR. X-ray diffraction and phenomenological studies of the engineered monoclinic crystal domains in single crystal relaxor ferroelectrics. *J Appl Phys* 2000;87:8159–64.
- [57] Noheda B, Cox DE, Shirane G, Park S-E, Cross LE, Zhong Z. Polarization rotation via a monoclinic phase in the piezoelectric 92% $\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3$ -8% PbTiO_3 . *Phys Rev Lett* 2001;86:3891–4.
- [58] Noheda B, Zhong Z, Cox DE, Shirane DE, Park S-E, Rehrig P. Electric field induced phase transitions in rhombohedral $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3$. *Phys Rev B* (submitted for publication). *Cond-mat/0201182*.
- [59] Ohwada K, Hirota K, Rehrig PW, Gehring PM, Noheda B, Fujii Y et al. Neutron diffraction study of the irreversible $\text{R-M}_A\text{-M}_C$ phase transition in single crystal $\text{Pb}[(\text{Zn}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x]\text{O}_3$. *J Phys Soc Jpn* 2001;70:2278–83.
- [60] Bellaiche L, Garcia A, Vanderbilt D. Electric-field induced polarization paths in $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ alloys. *Phys Rev B* 2001;64:060103/1–4.
- [61] Viehland D. Symmetry-adaptive ferroelectric mesostates in oriented $\text{Pb}(\text{Bi}_{1/3}\text{Bi}_{2/3})\text{O}_3$ - PbTiO_3 crystals. *J Appl Phys* 2000;88:4794–806.
- [62] Lu Y, Jeong D-Y, Cheng ZY, Zhang QM, Luo HS, Yin Z-W et al. Phase transitional behavior and piezoelectric properties of the orthorhombic phase of $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 . *Appl Phys Lett* 2001;78:3109–11.
- [63] Viehland D, Amin A, Li JF. Piezoelectric instability in $\langle 011 \rangle$ -oriented $\text{Pb}(\text{Bi}_{1/3}\text{Bi}_{2/3})\text{O}_3$ - PbTiO_3 crystals. *Appl Phys Lett* 2001;79:1006–8.
- [64] Ye Z-G, Noheda B, Dong M, Cox DE, Shirane G. A monoclinic

- phase in the relaxor-based piezo-/ferroelectric $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ – PbTiO_3 system. *Phys Rev B* 2001;64:184114/1–5.
- [65] Hirota K, Ye Z-G, Wakimoto S, Gehring P, Shirane G. Neutron diffuse scattering from polar nanoregions in the relaxor $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$. *Phys Rev B* 2002;65:104105/1–7.
- [66] Kiat J-M, Baldinozzi G, Dunlop M, Malibert C, Dkhil B, Menoret C et al. Anharmonicity and disorder in simple and complex perovskites: high energy synchrotron and hot neutron diffraction study. *J Phys Condens Matter* 2000;12:8411–25.
- [67] Burton B, Cockayne E. Why $\text{Pb}(\text{B},\text{B}')\text{O}_3$ perovskites disorder at lower temperatures than $\text{Ba}(\text{B},\text{B}')\text{O}_3$ perovskites. *Phys Rev B* 1999;60:R12542–5.
- [68] Fornari M, Singh DJ. Possible coexistence of rotation and ferroelectric lattice distortions in rhombohedral $\text{PbZr}_{1-x}\text{TiO}_3$. *Phys Rev B* 2001;63:092101/1–4.
- [69] Ranjan R, Ragini S, Mishra SK, Pandey D, Kennedy BJ. Antiferrodistortive phase transition in $\text{Pb}(\text{Zr}_{0.48}\text{Ti}_{0.52})\text{O}_3$: a powder neutron diffraction study. *Phys Rev B* 2002;65:060102/1–4.
- [70] Amin A, Newnham RE, Cross LE, Cox DE. Phenomenological and structural study of a low temperature phase transition in the PbZrO_3 – PbTiO_3 system. *J Solid State Chem* 1981;37:248–55.